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(54) **Silicon nitride sintered bodies and method of manufacturing the same.**

(57) Silicon nitride sintered bodies are disclosed which contain rare earth element compounds and silicon carbide, and in which the intergranular phases between the silicon nitride particles are substantially crystallized. To make such sintered bodies, rare earth element oxides and a silicon carbide powder raw material are used as additives when preparing raw powders and the intergranular phases are crystallized during a temperature descending stage following a firing. The silicon carbide achieves effective densification of structure of the sintered body and crystallization of the intergranular phases, thereby making it possible to provide sintered bodies having intergranular phases with little glass phase uncrystallized and having excellent high-temperature strengths.

EP 0 397 464 A1

SILICON NITRIDE SINTERED BODIES AND METHOD OF MANUFACTURING THE SAME

The present invention relates to silicon nitride sintered bodies having excellent mechanical strengths at high temperatures and to a method of manufacturing the same.

For production of silicon nitride sintered bodies containing oxides of IV a group elements including rare earth elements as additives, for example, in Japanese Patent Publication No. 48-7486, a manufacturing method of the sintered body is disclosed which comprises preparing a mixed powder consisting essentially of at least 85 mol% of silicon nitride powdery raw material and less than 15 mol% of at least one oxide selected from the oxides of III a group elements, shaping the thus prepared powder, and subjecting the resulting shaped-body to a firing under an inert atmosphere, and in Japanese Patent Publication No. 49-21091, the silicon nitride sintered body is also disclosed which consists of at least 50 wt% of Si_3N_4, less than 50 wt% of at least one oxide selected from Y_2O_3 and the oxides of La group elements, and 0.01~20 wt% of Al_2O_3.

However, it is difficult to obtain a sintered body having excellent high-temperature strength when adding only rare earth elements to the silicon nitride powdery raw material. On the other hand, when the sintered body contains Al_2O_3 as an additive, structure of the sintered body is progressively densified, but the softening point of its intergranular phase is lowered to considerably degrade the high-temperature strengths of the sintered body.

To obtain the sintered body having the excellent high-temperature strength, the applicant of the present invention, in Japanese Patent Publication No. 63-100067, discloses a technique which provides the sintered body with the excellent high-temperature strength by adding rare earth elements, having a predetermined composition and a predetermined weight ratio, to the silicon nitride powdery raw material and by specifying crystal phase of the sintered body.

In the silicon nitride sintered body disclosed in the Japanese Patent Publication No. 63-100067, it is possible to improve the high-temperature strength of the sintered body to a certain extent, but it is still lower than a room-temperature strength thereof. The result is interpreted as follows. Even performing crystallization of grain boundaries of the sintered body still leaves a some amount of uncrystallized glass phase when adopting the composition disclosed in the publication. For lowering a residual amount of the uncrystallized glass phase, it is possible to propose a manufacturing method comprising a powdery raw material in which little glass phase remains in the grain boundaries by enlarging a molecule ratio of the added oxides of the rare earth elements with respect to an amount of SiO_2, to which a whole amount of oxygen contained in the silicon nitride powdery raw material is converted. However, the method makes it difficult to sufficiently densify structure of the sintered body.

It is an object of the present invention to eliminate the drawbacks mentioned above, and to provide silicon nitride sintered bodies which may have substantially the same strength at high temperatures as at room temperature and a method of manufacturing the same.

The present invention provides silicon nitride sintered bodies, which are consisting essentially of silicon nitride, at least one compound of a rare earth element and silicon carbide and in which intergranular phases between silicon nitride particles contained in the sintered bodies are substantially composed of crystal phases.

Besides, the present invention provides a method of manufacturing silicon nitride sintered bodies which comprises:
preparing a powder consisting of powdery raw materials of silicon nitride, at least one oxide of a rare earth element and silicon carbide,
shaping the thus prepared powder to obtain a shaped-body,
subsequently subjecting the shaped-body to a firing under an N_2 atmosphere, and
substantially crystallizing intergranular phases between silicon nitride particles during a temperature-descending stage following the firing.

In the above mentioned construction, the following effects are found: Namely, the present invention, which comprises adding a silicon carbide powder to the silicon nitride powdery raw material containing the oxide(s) of selected rare earth element(s), shaping the resulting powder and firing the thus obtained shaped-body under the N_2 atmosphere to crystallize the shaped-body, thereby making it possible to provide the sintered body containing silicon carbide with the intergranular phases between silicon nitride particles substantially forming crystal phases and to substantially eliminate residual glass phases in grain boundaries in the silicon nitride sintered body. Thereby it becomes possible to provide the sintered body with the excellent high-temperature strength substantially equal to the room- temperature strength thereof.

Namely, if an amount of the oxides of rare earth elements added to the silicon nitride powdery raw material, which contains the silicon carbide

powder as an additive and a certain amount of oxygen, is larger than a predetermined amount of the oxides thereof, which provides the resulting sintered body with the most excellent high-temperature strength when the powdery raw material contains no silicon carbide powder and the above certain amount of oxygen, it is possible to sufficiently densify the structure of the sintered body by adding the silicon carbide powder, which also achieves effective crystallization of the grain boundaries. Consequently, it is possible to obtain the silicon nitride sintered body, having the crystallized intergranular phase with very little glass phase and excellent high-temperature strength. Besides, the certain amount of oxygen contained in the silicon nitride powdery raw material is indicated in its converted SiO_2 amount. Moreover, the above predetermined amount of the oxides of rare earth elements, which provides the sintered body with the most excellent high-temperature strength when no silicon carbide powder is added, differs according to the silicon nitride powdery raw material used. If the amount of the oxides of rare earth elements added to the powdery raw material is not larger than the predetermined amount of the oxides thereof, it is possible to proceed the densification of the structure of the sintered body without adding the silicon carbide powder. However, it becomes possible to proceed crystallization of grain boundaries, and consequently to obtain the silicon nitride sintered body having intergranular phases with little glass phase and the excellent high-temperature strength by adding the silicon carbide powder.

An amount of oxygen in the silicon nitride powdery raw material is preferably 1~3 wt%. The amount of oxygen can be controlled by oxidizing the silicon nitride powdery raw material, or by adding a silicon oxide powder thereto.

A total amount of oxides of rare earth elements as additives is preferably 2.7~10 mol%. The reason is as follows: If the total amount is lower than 2.7 mol%, it is impossible to obtain a liquid phase to sufficiently proceed the densification, if the total amount is higher than 10 mol%, it exhibits a tendency to make the densification difficult even when adding the silicon carbide powder. Besides, it is possible to use Lu_2O_3, Tm_2O_3, Er_2O_3, etc. as the oxides of rare earth elements 26 other than Y_2O_3, Yb_2O_3 to take substantially same effects. An amount of rare earth elements contained in the resulting sintered body is the same as that of the elements contained in the starting powdery raw material. The amount of the oxides of rare earth elements (indicated by mol%) is calculated as (the amount of the oxides of rare earth elements indicated by mol)/(a sum of the amount of the oxides of rare earth elements and silicon nitride, both indicated by mol).

The amount of the silicon carbide powder as an additive is preferably 0.1~11 wt% with respect to an amount of a formulated powder consisting of silicon nitride and the oxides of rare earth elements. When the amount of the silicon carbide powder is smaller than 0.1 wt%, it is impossible to sufficiently densify the structure of the sintered body and effectively proceed the crystallization. On the other hand when the amount is larger than 11 wt%, silicon carbide may occasionally inhibit the densification. The amount of the silicon carbide powder is more preferably 0.5~7 wt%. The amount of silicon carbide contained in the sintered body may be reduced a little compared to the amount of the silicon carbide powder formulated into the raw material. Moreover, α-type, β-type and amorphous silicon carbide may be used as appropriate, respectively.

In the method of manufacturing silicon nitride sintered bodies according to the invention, first the formulated powdery raw material is prepared by mixing the silicon nitride powder, the powder of the oxide of each rare earth element and the silicon carbide powder. Next, the thus prepared mixture is shaped to a predetermined shape to produce the shaped-body. Subsequently, the resulting shaped-body is subjected to the firing at a temperature of 1700~2100°C, preferably 1900~2000°C, under the N_2 atmosphere at a normal pressure or a high pressure according to the firing temperature, and the intergranular phases are substantially crystallized during the following temperature-descending step. Consequently, there is obtained the silicon nitride sintered body according to the invention having the intergranular phases between silicon nitride particles, which is substantially crystallized and contains very little glass phase.

For a better understanding of the invention, reference is taken to the accompanying drawing, in which:

Fig. 1. is a photograph showing microstructures of the sintered body according to the invention.

Hereinafter, actual embodiments according to the invention will be described.

A silicon nitride powder having a purity of 97 weight %, an oxygen content of 2.2 weight %, an average grain diameter of 0.6 µm and BET specific surface area of 17 m^2/g, additives described in Table 1, each additive having a purity of 99.9 weight %, an average grain diameter of 0.3~2.5 µm, and a silicon carbide powder having a purity of 99 weight %, an average grain diameter of 0.4 µm and BET specific surface area of 20 m^2/g are mixed and formulated in the proportions as described in Table 1. Then, by using media made of silicon nitride porcelain and a nylon resin vessel having an inner volume of 1.2 ℓ, 1.8 kg of media and 300 mℓ of water were added to 200 g of the

formulation raw material, which was ground by a vibration mill at a vibration rate of 1200 times/min for 3 hours. Subsequently, the water was removed to obtain dry powders, which were further granulated to have a grain diameter of 150 µm. The thus obtained powders were isostatic-pressed under a pressure of 7 ton/cm^2 to obtain shaped bodies having dimensions of 50x40x6 mm, which were then fired according to the firing conditions as described in Table 1 to provide silicon nitride sintered bodies Nos. 1~27 according to the invention. Besides, by using the same silicon nitride raw materials as described above, formulated powdery raw materials were obtained by adopting additives and formulated ratios as described in Table 1. Then, the resulting formulated powdery raw materials were ground, granulated and shaped as described above, and the resulting shaped bodies were then subjected to the firing in the firing conditions as described in Table 1 to obtain the sintered bodies according to comparative embodiment Nos. 28~31. Besides, in the comparative example Nos. 29 and 30, the crystallization was performed by a reheating treatment.

Bulk densities, four point bending strengths at a room temperature and 1400°C of the sintered body were measured and the intergranular crystal phases thereof were detected. The experimental results were shown in Table 1, in which the bulk densities of the sintered bodies were measured by Archimedes method and indicated as values relative to theoretical densities calculated from the compositions and densities of the formulated powders. The densities of the formulated powders were calculated by adopting the following values; Si_3N_4: 3.2 g/cm^3, Y_2O_3: 5.0 g/cm^3, Yb_2O_3: 9.2 g/cm^3, Tm_2O_3: 8.8 g/cm^3, Lu_2O_3: 9.4 g/cm^3, Er_2O_3: 8.6 g/cm^3, SiC: 3.2 g/cm^3. The four point bending strengths were measured according to "a testing method of bending strengths of fine ceramic materials (JIS R-1601)". The intergranular crystal phases were detected by performing X-ray diffraction test using CuKα-ray. In Table 1, J is used to mean a crystal phase having a caspidine structure, which have the same type diffraction curve as that of $Si_3N_4 \cdot 4Y_2O_3 \cdot SiO_2$ shown in JCPDS card No. 32-1451 and in which the crystallographic position of Y can be replaced or occupied by the other rare earth elements. H is used to mean a crystal phase having an apatite structure, which have the same type diffraction curve as that of $Si_3N_4 \cdot 10Y_2O_3 \cdot 9SiO_2$ shown in JCPDS card No. 30-1462 and in which the crystallographic position of Y can be replaced or occupied by the other rare earth elements. K is used to mean a crystal phase having an wollastonite structure, which have the same type diffraction curve as that of $2Y_2O_3 \cdot SiO_2 \cdot Si_3N_4$ shown in JCPDS card No. 31-1462 and in which the crystallographic position of Y can be replaced or occupied by the other rare earth elements. L is used to mean a crystal phase indicated as Re_2SiO_5 (Re: rare earth elements), which have the same type diffraction curve as that shown in JCPDS card No. 21-1456, 21-1458, 21-1461, 22-992 or 36-1476. S is used to mean a crystal phase indicated as $Re_2Si_2O_7$ (Re: rare earth elements), which have the same type diffraction curve as that shown in JCPDS Card 20-1416, 21-1457, 21-1459, 21-1460, 22-994 or 22-1103.

Moreover, in Table 1, ratios of intergranular crystal phases were also shown, and they were detected by an integrated value of the strength peak of respective intergranular phases other than β-Si_3N_4.

Further, in Fig. 1, a SEM photograph of the sintered body No. 4 according to the invention was shown. In Fig. 1, A shows β-Si_3N_4 particles, B shows intergranular phases and C shows SiC particles.

Table 1(a)

	No.	Oxides of rare earth elements (wt%)			Total amount of the oxides (mol%)	SiC (wt%)	Temperature (°C)	Time (hr)	Pressure (atm)	Relative density (%)	Room-temperature strength (MPa)	Strength at 1400°C (MPa)	Intergranular crystal phase
		Y_2O_3	Yb_2O_3	The other									
Present invention	1	3.4	14		7.8	0.1	1900	2	10	97	770	750	J:H=50:50
	2	3.4	14		7.8	0.5	1900	2	10	99	800	800	J:H=60:40
	3	3.4	14		7.8	1	1900	2	10	99	810	810	J:H=70:30
	4	3.4	14		7.8	5	1900	2	10	99	810	810	J=100
	5	3.4	14		7.8	7	1900	2	10	98	800	800	J=100
	6	3.4	14		7.8	11	1900	2	10	97	770	760	J=100
	7	2	9		4.7	0.5	1900	2	10	99	780	770	H=100
	8	2	9		4.7	1	1900	2	10	99	790	780	H=100
	9	2	9		4.7	3	1900	2	10	99	790	790	H:J=60:40
	10	2	9		4.7	7	1900	2	10	98	780	780	J:H=60:40
	11	2	9		4.7	1	2100	2	100	99	780	750	J:H:K=50:40:10
	12	2	7		3.9	1	1900	2	10	98	730	700	H:S=70:30
	13	2	7		3.9	3	1900	2	10	98	710	700	H=100
	14	2	4		2.7	1	1900	2	10	97	680	670	L:S=70:30
	15	0	15		5.9	3	1700	3	1	97	780	770	J=100
	16	10	0		6.4	1	1950	2	50	98	800	800	J:H=80:20
	17	4.2	17		10	2	1900	2	10	97	760	760	J=100

Table 1(b)

	No.	Oxides of rare earth elements (wt%)			Total amount of the oxides (mol%)	SiC (wt%)	Temperature (°C)	Time (hr)	Pressure (atm)	Relative density (%)	Room-temperature strength (MPa)	Strength at 1400°C (MPa)	Intergranular crystal phase
		Y_2O_3	Yb_2O_3	The other									
Present invention	18	3.8	15		8.8	2	1900	2	10	98	800	800	J=100
	19	2.6	11		5.8	1	1900	2	10	98	800	790	J:H=60:40
	20	0	19		7.8	1	1900	2	10	99	810	800	J=100
	21	5.8	10		7.8	1	1900	2	10	98	800	790	J=100
	22	3.4	14		7.8	1	2000	2	100	99	810	800	J=100
	23	3.4	14		7.8	1	1950	2	15	99	810	810	J=100
	24	3.4	14		7.8	1	1800	3	10	97	770	760	J:H=80:20
	25	2	0	Tm_2O_3 9	4.7	7	1950	2	20	98	760	760	H:L=60:40
	26	0	7	Lu_2O_3 7	4.6	3	1900	2	10	98	780	780	J=100
	27	2	0	Er_2O_3 13	6.6	1	1900	2	10	99	800	800	J=100
Comparative examples	28	3.4	14		7.8	0	1900	6	10	90	400	300	** J:H:L=40:40:20
	29	2	9		4.7	0	1900	2	10	98	700	650	H:S=70:30 *
	30	2	7		3.9	0	1900	2	10	98	730	620	H:S=60:40 *
	31	4.2	17		10	0	1900	6	10	80	-	-	J=100 **

(Note) * Intergranular phases were crystallized by performing the reheating treatment.

** not sufficiently densified

J : Caspidine structure H : Apatite structure

K : Wollastonite structure L : Re_2SiO_5 (Re: rare earth elements)

S : $Re_2Si_2O_7$ (Re: rare earth elements)

As clearly shown in Table 1, the sample Nos. 1~6 according to the invention, which contains relatively large amount of the oxides of rare earth elements and further silicon nitride as additives, had high relative densities of more than 97% and high strengths at the high temperature, which was only a little different from the room-temperature strengths. On the contrary, structure of the comparative sample No. 28 containing no silicon carbide as an additive was not sufficiently densified. The results demonstrate that the silicon carbide additive proceeds the densification of the structure effectively.

For example, the sample Nos. 8, 12 according to the invention, in which the amounts of the oxides of rare earth elements as additives were relatively low and the grain boundaries were crystallized to principally form H phases by adding silicon carbide, had higher strengths at the high temperature compared to that of the comparative sample Nos. 29, 30, in which no silicon carbide was added and the grain boundaries were crystallized by performing the reheating treatment. In this case, silicon carbide as an additive effectively proceeds the crystallization of the grain boundaries to effectively reduce the residual glass phase therein rather than the densification of the structure of the sintered body.

As can be seen from the above explanation, in the silicon nitride sintered body and the manufacturing method thereof according to the present invention, because silicon carbide is added to the silicon nitride powder containing predetermined oxide of each rare earth element and the thus obtained formulated powdery raw material is shaped to form the shaped body which is then subjected to the firing under the N_2 atmosphere and crystallized, it is possible to provide the sintered body containing silicon carbide, in which the intergranular phases between silicon nitride particles are substantially crystallized and the high-temperature strength of the sintered body is comparable to the room-temperature strength thereof.

Claims

1. A silicon nitride sintered body, which consists essentially of silicon nitride, at least one compound of at least one rare earth element and silicon carbide and in which intergranular phases between the silicon nitride particles are substantially composed of crystal phases.

2. A silicon nitride sintered body as claimed in claim 1, in which said rare earth element(s) are/is Y and/or Yb.

3. A silicon nitride sintered body consisting essentially of silicon nitride as predominant component and minor amounts of additive componets in the form of

(a) a rare earth element compound or compounds in an amount selected to increase the high temperature strength of the silicon nitride and

(b) silicon carbide in an amount selected to achieve crystallization of intergranular phases between the silicon nitride particles.

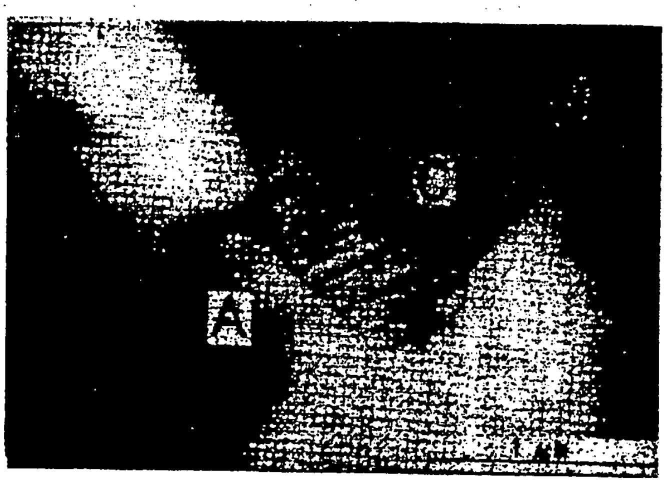
4. A silicon nitride sintered body according to claim 3 wherein the amount of rare earth element compound or compounds is in the range 2.7 to 10 mol% based on the total amount of silicon nitride and rare earth element compounds.

5. A silicon nitride sintered body according to claim 3 or claim 4 wherein the amount of silicon carbide is in the range 0.1 to 11 wt%.

6. A method of manufacturing a silicon nitride sintered body which comprises:
preparing a powder consisting of powdery raw materials of silicon nitride, at least one oxide of at least one rare earth element and silicon carbide,
shaping the thus prepared powder to obtain a shaped body,
subsequently subjecting the shaped-body to a firing under an N_2 atmosphere, and
substantially crystallizing intergranular phases between silicon nitride particles during a temperature-descending stage following the firing.

7. A method as claimed in claim 6, in which said rare earth element(s) are/is Y and/or Yb.

FIG_1



A: β- Si_3N_4

B: Intergranular Phase

C: SiC

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4980

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CHEMICAL ABSTRACTS, vol. 111, no. 6, 7th August 1989, page 312, abstract no. 44244x, Columbus, Ohio, US; & JP-A-01 09 872 (NISSAN MOTOR CO., LTD) 13-01-1989 ---	1-7	C 04 B 35/58
A	EP-A-0 080 711 (TOKYO SHIBAURA DENKI K.K.) * Claims 1,6,7; examples 6,16 * -----	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 04 B 35/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-07-1990	HAUCK, H.N.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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